

LDWSF  
12.3.5501

## Tributyltin Paint—the Navy Perspective

Soapbox

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Tributyltin, also known as TBT or organotin, has been in use since the 1960s as a very effective biocide. Because of its known effectiveness, the Navy began over 25 years ago looking into the use of TBT paints as an antifouling coating on our ships' hulls.

Fouling on the hull of a boat or ship, as any sailor knows, is a constant frustration, requiring scraping and repainting periodically to maintain a smooth clean surface. For the Navy, with ships having wetted hull areas as great as 150,000 square feet, maintaining a fouling-free surface becomes a monumental task.

In tropical areas, Navy ships may begin to experience significant fouling in less than a year when painted with the currently used copper-based paints. Navy ships painted experimentally with organotin paints, on the other hand, have gone as long as six years and remained essentially free of fouling.

Add to this the fact that the Navy would save the taxpayer about \$100 million per year in fuel costs, reduce wear on propul-

sion machinery, and decrease downtime for hull cleanings if we painted the fleet with TBT paints.

Now, when you think of the significance of this in relation to the Navy's mission to patrol the high seas and keep the sea lanes of the world free, one can readily see why the Navy began to look more closely at the use of TBT.

The Navy has been carefully studying the fates and effects of TBT in the marine environment for over ten years.

By 1983, it was evident that TBT leach rates from paints were highly variable and the Navy decided to consider only the low-leach-rate paints registered by the Environmental Protection Agency. The Navy environmental assessment (EA) on TBT paints established the TBT leach rate of 0.1 micrograms per square centimeter per day to meet the conservative Navy water quality standard of 50 parts per trillion (no EPA water standard exists).

The environmental assessment used a TBT decay rate of 2% per day; new research has shown the TBT decay rate to be about 10% per day, which means that TBT is not a persistent chemical like DDT or Kepone. It dissipates quickly.

Also significant is the fact that higher orders of marine life, such as crustaceans and fish, are able to degrade TBT by enzymes in their digestive system. Only bivalves are sensitive, and then the measured acute toxicity is in the hundreds range of parts per trillion with chronic effects well above 50 parts per trillion.

The ability of marine life to depurate and degrade TBT is a positive indicator of low risk of TBT accumulation in the food chain.

But the key to this is use of low-leach-rate paints—most paints in use have a much higher leach rate than the 0.1 micrograms per square centimeter per day required

by the Navy for steel hulled ships. If the Navy were to paint the entire fleet with TBT paints using our leach rate, we would contribute only 268 kilograms of TBT per year to the environment. Contrast that to the current contribution of pleasure craft in the United States of 7620 kilograms/year; commercial ships, 3965 kilograms/year; and the U.S. fishing fleet 1302 kilograms/year. Monitoring on non-Navy harbors and marinas has shown TBT levels in the water as high as 500 parts per trillion due to the use of high release rate TBT paints.

Despite this load of TBT in our environment, there are no documented cases of environmental damage in U.S. coastal waters from TBT usage. Reducing the TBT burden in coastal waters to 20%-50% of the present values is easily possible merely by setting a limit on paint leach-rates. Such action should remove environmental concerns if supplemented by selective monitoring to a national TBT water standard.

The Navy will continue to comply with regulations that apply to all ships and crafts uniformly, but we do not support the Navy being singled out as the only entity not permitted to use TBT paints. It is particularly ironic that the Navy should be singled out when it is the Navy that has done by far the most extensive testing to ensure the environment would not be harmed by usage of TBT paints and is virtually the only organization to specify paints with extremely low release rates.

If the entire Navy were painted with TBT, 268 kilograms/yr. of TBT would be added to the waters, which represents 2% of the current contribution.

The real answer to reducing TBT in coastal waters is to require all users of TBT to use only low-release paints. /st/

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*Copy of  
journal changes made  
6/23/87*

Measuring Tri-n-Butyltin in Salmon by Atomic Absorption: Analysis  
With and Without Gas Chromatography

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As marine pollutants, tri-n-butyltin (TBT) compounds are the focus of increased concern. They are very toxic to marine fouling organisms (Hall and Pinkney 1985) and very effective as active ingredients in anti-foulant preparations. Yet, at concentrations of  $< 1 \mu\text{g/L}$ , they also are toxic to non-target organisms (Hall and Pinkney 1985). Concern over adverse effects on non-target organisms has resulted in regulations restricting their use in France and in the United Kingdom and has delayed their use by the U.S. Navy on its fleet (Champ 1986).

Limited information on the persistence of TBT compounds accumulated by marine fauna is partly due to the difficulty of chemical analysis. Analytical methods must be sensitive and specific; TBT concentrations well below  $1 \mu\text{g/L}$  may exert deleterious effects, and TBT compounds are much more toxic to aquatic fauna than are most other organotin compounds. The most sensitive analytical methods, which are suitable for environmental samples, typically rely on 1) chemical derivatization to increase organotin vapor pressure, 2) separation from coextractives by gas chromatography, and 3) measurement of tin in the gas chromatograph effluent by a tin-selective detector (Meinema et al. 1978; Jackson et al. 1982; Maguire and Tkacz 1983). These methods, although expensive to perform, specifically identify organotins at a high degree of quantitative sensitivity. Less expensive methods do not provide specific identification, but may be useful if they reliably identify, for further analysis by more expensive methods, environmental samples that may contain TBT. Such screening methods should be relatively inexpensive and at least as sensitive as the more elaborate method. The basis of the screening method examined herein is the graphite furnace atomic absorption spectrophotometry of organic extracts proposed by Dooley and Vafa (1986).

This paper compares two methods--one specific for TBT and the other not. It also examines whether TBT is the organotin compound detected by the screening method used in Short and Thrower (1986), who raised juvenile chinook salmon (Oncorhynchus tshawytscha) in TBT-treated sea pens.

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## MATERIALS AND METHODS

Thirty salmon from a previous study on TBT exposure by Short and Thrower (1986) were selected for analysis. Of these fish, 12 were chinook salmon reared in sea pens treated with TBT anti-foulants: 8 fish for 13 continuous months and 4 fish for 19 continuous months. Five of the 30 fish were juvenile chinook salmon that had not been exposed to TBT-treated sea pens and served as controls. The remaining 13 fish were adult chinook salmon, silver salmon (*O. kisutch*), and Atlantic salmon (*Salmo salar*) that were advertised as products of aquaculture and were purchased from fish markets in Seattle, Washington, and Portland, Oregon.

These fish were stored at -20°C for up to 2 mo [for further details, see Short and Thrower (1986)] prior to analysis. From each fish, 5 g of muscle tissue was dissected; care was taken not to include any skin, adipose tissue, or portions of the lateral line. The dissected tissue was digested with concentrated HCl, and the digest was extracted with hexane.

The hexane extracts were analyzed by two methods. The first was a simple screening method (Short and Thrower 1986). The hexane extract was evaporated to dryness at 20°C with a rotary evaporator. The residue was dissolved in a solution consisting of 0.1 mL of concentrated nitric acid and 4.9 mL of glacial acetic acid. This solution was analyzed for total tin content by flameless atomic absorption spectrophotometry with a Perkin-Elmer model 5000 atomic absorption spectrophotometer equipped with a Zeeman background corrector. The manufacturer's suggested instrument settings were used for the analysis, and the method of standard additions was used to estimate concentrations of tin in the nitric/acetic acid solution. The overall detection limit of this method was about 5 ng TBT/g of muscle tissue (wet weight).

More elaborate than the screening method, the second method [adapted from Maguire et al. (1986)] analyzed the hexane extracts by employing a gas chromatograph with an atomic absorption (GCAA) spectrophotometer as a detector. The hexane extract was reduced in volume and added to a Grignard reaction mixture to pentylate the TBT with 1-pentylmagnesium bromide. After pentylation, the Grignard reaction was stopped with sulfuric acid, and the reaction mixture was extracted with hexane. A known amount of tetrabutyltin was added to this hexane extract as an internal standard. The extract was reduced in volume with a rotary evaporator to about 2 mL and eluted through a 3% deactivated silica gel (200-325 mesh, Silica Gel, Davison Chemical) column with hexane. The hexane eluate was reduced in volume to about 0.2 mL just prior to analysis. This concentrated eluate was injected into a Hewlett-Packard 5880A gas chromatograph equipped with a fused silica capillary column and interfaced with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer.

Briefly, the GCAA method employs 1) separation of TBT by gas chromatography, 2) reduction of TBT to metallic tin by a

hydrogen-rich flame in a quartz tee, and 3) atomic absorption spectrophotometric determination of the vaporized tin. The capillary column adaptation consisted of extending the column to within 1.8 cm of the horizontal segment of the quartz tee and sweeping the transfer line with the hydrogen stream. The column was a dimethyl silicone capillary column (length, 12 m; internal diameter, 0.2 mm; film thickness, 0.33  $\mu\text{m}$ ). Inlet pressure of the nitrogen carrier gas was 140 kPa, and the instrument was run in the splitless mode. Oven temperature program was 100°C initial temperature for 1 min, 30°C/min temperature ramp for 2 min to 160°C, then 4°C/min temperature ramp for 7 min to 188°C. Inlet temperature was 225°C; the transfer line was maintained at 200°C. Hydrogen and air flow rates used were 100 and 130 mL/min, respectively. These modifications to the method used by Maguire and Tkacz (1983) resulted in a detection limit of about 100 pg of tin. The overall detection limit was 15 ng TBT/g muscle tissue (wet weight).

By both methods, recoveries of TBT added to uncontaminated chinook salmon muscle tissue were between 87 and 101%. The identification of TBT for the GCAA method was based on the retention times of added TBT and the specificity of the detector for metallic tin. Addition of TBT and tetrabutyltin to uncontaminated muscle tissue resulted in no extraneous peaks. Results of both methods were tested for significant differences by analysis of variance.

## RESULTS AND DISCUSSION

All of the salmon reared in TBT-treated sea pens, but none from the untreated sea pen, contained readily detectable concentrations of TBT in muscle tissue (Table 1). As determined by the GCAA method, average TBT concentrations were 0.71 and 0.46  $\mu\text{g/g}$  muscle tissue of salmon exposed to TBT for 13 and 19 mo, respectively.

Table 1. Analysis for TBT in chinook salmon by the GCAA and screening methods; data on screening method are from Short and Thrower (1986).

Exposure (mo)	<u>n</u>	TBT ( $\mu\text{g/g}$ muscle tissue)	
		GCAA	Screening method
0	5	ND	ND
13	8	0.71 $\pm$ 0.17	0.82 $\pm$ 0.05
19	4	0.46 $\pm$ 0.23	0.90 $\pm$ 0.10

ND = none detected [detection limit is  $\leq 15$  ng TBT/g muscle tissue (wet weight)].

The screening method correctly identified all 21 salmon that contained TBT as determined by the GCAA method, and generally gave comparable quantitative results. The screening method gave no

false positive or false negative identifications, although the TBT concentrations estimated were somewhat higher than those estimated by the GCAA method. The two methods did not significantly differ in TBT concentrations in the muscle tissue of salmon exposed to TBT for 13 mon ( $P = 0.95$ ; Table 1), thus verifying the conclusions of Short and Thrower (1986) that salmon reared in TBT-treated sea pens for less than 1 year can accumulate TBT in muscle tissue.

Conversely, the GCAA method measured significantly lower TBT concentrations in salmon exposed 19 mo than did the screening method. With the GCAA method, no other organotins were eluted from these samples; it is hypothesized that hexane extracts of these samples contained organotin compounds which, after pentylation, were not eluted from the silica gel column. Such compounds may have been the result of catabolism of TBT in salmon exposed for 19 mo.

The TBT concentrations in the muscle tissue of salmonids advertised as aquaculture products and purchased from U.S. fish markets were not significantly different when analyzed by the GCAA and screening methods ( $P = 0.95$ ; Table 2); this agrees with the results of Short and Thrower (1986), who suggested that TBT is present in the flesh of some aquacultured salmonids in the U.S. marketplace. These results also support their hypothesis that these TBT burdens were acquired during residence in TBT-treated sea pens.

Table 2. Analysis for TBT in salmonids advertised as aquaculture products purchased from fish markets in Seattle, Washington, and Portland, Oregon, by the GCAA and screening methods. Data on the screening method are from Short and Thrower (1986).

Species	<u>n</u>	TBT ( $\mu\text{g/g}$ muscle tissue)	
		GCAA	Screening method
Seattle			
Silver salmon	1	0.17	$0.20 \pm 0.11$
Silver salmon	1	ND	ND
Chinook salmon	2	ND	ND
Atlantic salmon	3	$0.069 \pm 0.121$	$0.081 \pm 0.031$
Atlantic salmon	1	ND	ND
Portland			
Silver salmon	5	$0.098 \pm 0.042$	$0.074 \pm 0.012$

ND = none detected [detection limit is  $\leq 0.015$  ng TBT/g muscle tissue (wet weight)].

The screening method has a tendency to overestimate TBT concentrations in the flesh of salmon, compared with corresponding GCAA results. Although not desirable, it is preferable to a tendency toward underestimation. Thus, the screening method in this study may have merit for identifying biological samples for more critical analysis for TBT.

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Received May 26, 1987; accepted June 17, 1987.